RT-VARIATION OF THE PHOTOCHROMIC PROPERTIES OF SPIROOXAZINE TRAPPED IN ORGANIC-INORGANIC HYBRID MATRICES IN THE COURSE OF THE SOL-WETGEL-XEROGEL TRANSFORMATION

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Abstract

In a photochromic system host matrices significantly affect the photochromic properties of the encapsulated organic dye. They must be prepared at temperatures considerably below the decomposition point of the dye, and they should have sufficient free volume for the structural rearrangement to take place. The low-temperature, wet-chemical characteristics of sol-gel process and the pore structure of the gels make these requirements excellently satisfied.

In this work, organically modified silanes, ethyltrimethoxysilane (ETMS) and 3-glycidyloxypropyltrimethoxysilane (GPTMS) are used as starting materials to prepare gels doped with spirooxazine. Room temperature (RT)-variation of the photochromic properties in the organic-inorganic hybrid matrices (OIHM) containing NaF or bisphenol-A (BPA) is monitored during the sol-wetgel-xerogel transformation process.

Without the addition of BPA, both the photochromic intensity (ΔA_0) and the half-life time ($t_{0.5}$) decrease and level off in the wetgel-xerogel stage, while with the addition of BPA they increase and level off in the wetgel-xerogel stage. These results are discussed in terms of viscosity growth, pore structure formation, increase of polarity and steric hindrance.

Introduction

Preparation and characterization of solid photochromic materials have been an active area of intensive research because of the attracting potential applications. Organic photochromism resulted from photoinduced molecular rearrangement (ring opening-closure), e.g. spirooxazine, is of most importance to practical applications. Steric restriction imposed by the solid host matrices on the molecular rearrangement strongly affect the photochromic properties. Therefore, two main requirements should be satisfied for the matrices. They must be prepared at a temperature considerably below the decomposition point of the dye, and they should have sufficient free volume for the ring opening-closure reaction to take place.

Sol-gel processing offers a low-temperature approach to the preparation of solid materials. The porous structure of the sol-gel derived solids is favourable to the entrappment of dyes. It is obvious that the final pore size in the xerogels must be comparable to or greater than the dimensions of the dye molecules (in the range of 1-10 nm) so that the native structure can survive the shrinkage of the gels during drying and the photochromism can remain undegraded. Previous research work by other authors[1-3], however, show little satisfactory results in this connection. Photochromic dyes doped in certain sol-gel derived gels would either lose their photochromic activity rapidly or change into reverse photochromism even during the sol-wetgel transformation stage.

The purpose of this work is to develop suitable solid matrices for spirooxazine dyes via sol-gel processing, aiming to maintain high enough photochromic intensity in xerogels. We used two organically modified silanes, ethyltrimethoxysilane (ETMS) and 3-glycidyloxypropyltrimethoxysilane (GPTMS), as starting materials, with the addition of NaF or bisphenol-A (BPA) in the preparation of sols and investigated the variation of the photochromic properties in the course of the sol-wetgel-xerogel transformation. Our experimental results suggest that high enough photochromic intensity and satisfactory fading speed can be achieved up to the xerogel stage, especially when BPA is introduced into the composition at a sufficient content.

Experimental

Sol were prepared via the sono sol-gel process described in a previous paper of ours[4]. Water is added in the form of 0.1 N HNO_3 at the molar ratio of 1.5 to the silanes ($MR_{H_2O} = 1.5$). The concentration of NaF is $MR_{NaF} = 2x10^{-4}$. Different content of BPA ($MR_{BPA} \leq 0.30$) is used to establish its effect on the photochromic property. Viscous sols were poured into plastic cells of 4 mm optical path and kept open to allow evaporation of alcohols generated by hydrolysis under sonication. The home-made apparatus[5] was used for the measurement of photochromism. The photochromic intensity (ΔA_0) expressed by the absorbance at the photostationary state of the sample under UV irradiation, and half-life time ($t_{0.5}$) of the coloured form, i.e. the time length required for the photochromic intensity to decay to its half value, are evaluated from the transmission vs. fading time curves by a personal computer.

Results and discussion

The variation of ΔA_0 and $t_{0.5}$ of spirooxazine (1,3,3-trimethyl-spiro[indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine]) in OIHM-EG37 without and with NaF during the sol-wetgel-xerogel transformation are shown in Figs. 1 and 2, respectively. The following results can be drawn from these figures: (1) ΔA_0 decreases rapidly in the beginning stage, followed by a continous decreasing at a much slower speed, and levels off after 200 h ($MR_{NaF} = 2x10^{-4}$) or 400 h (no NaF is added), (2) $t_{0.5}$ increases in the early stage (< 100 h), then decreases and levels off in a similar way as ΔA_0.

In the early stage, the viscosity of the sol increases gradually due to the increase in the extent of condensation. As a result, a greater and greater portion of dye molecules are more and more tightly confined and even completely blocked to undergo colour change, so that the possibility of photochromic transformation decreases gradually in a statistical sense. On the other hand, the fading speed of the coloured form of the dye molecules which still remain photochromically active, decreases due to the increasing hindrance resulted from viscosity increase. At the gel point, a certain portion of dye molecules has been „killed“ and lose their photochromic activity. Only those dye molecules caged in the pores remain photochromically active and they are as free as in ethanol. Therefore, in the xerogel matrix both ΔA_0 and $t_{0.5}$ reach a steady value.

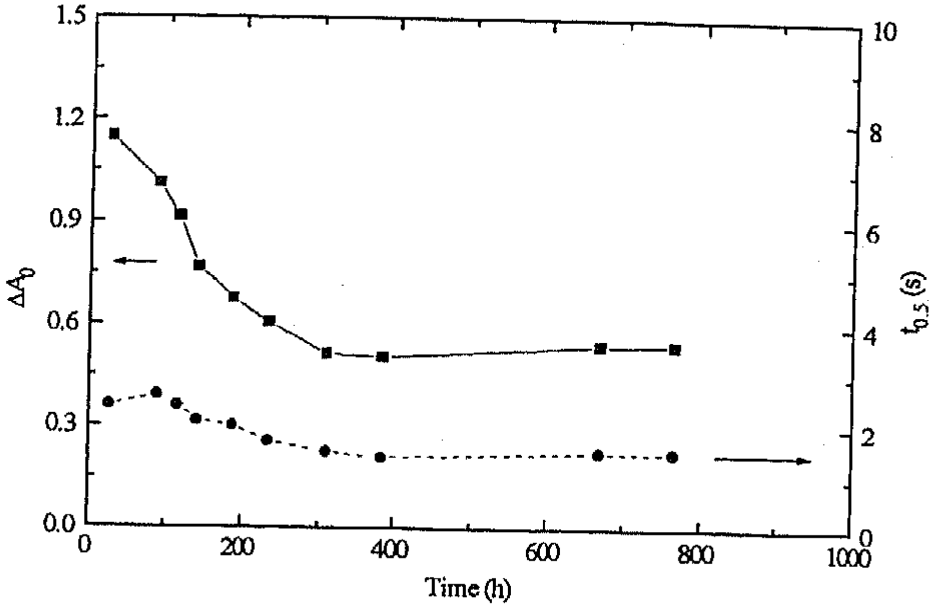

Fig. 1 Variation of photochromic intensity (ΔA_0) and half-life time ($t_{0.5}$) of spirooxazine in OIHM-EG37 during the sol-wetgel-xerogel transformation

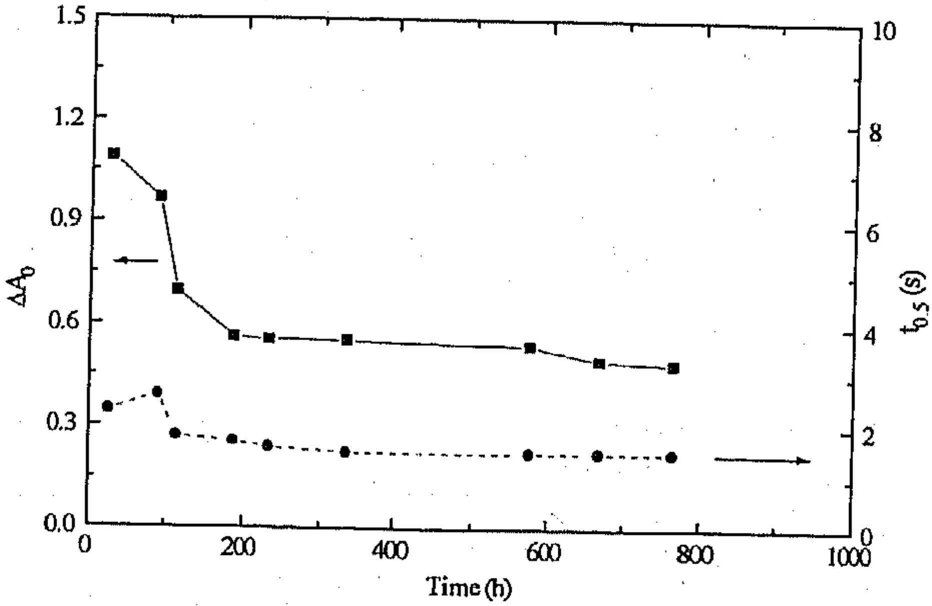

Fig. 2 Variation of photochromic intensity (ΔA_0) and half-life time ($t_{0.5}$) of spirooxazine in OIHM-EG37 ($MR_{NaF} = 2x10^{-4}$) during the sol-wetgel-xerogel transformation

This value of ΔA_0 depends on matrix composition while that of $t_{0.5}$ is similar to the ethanol solution ($t_{0.5}$ = 1.5 s), independent of matrix composition. In Fig. 3 ΔA_0 in OIHM-EG gels is presented as a function of composition in the ETMS-GPTMS system at various time points during the sol-wetgel-xerogel transformation. It can be seen that in the beginning (sol) stage (< 100 h) ΔA_0 exhibits only a slight decrease with increasing GPTMS content. The decrease tendency becomes more obvious in the middle (sol-wetgel) stage (< 200 h), and in the final (wetgel-xerogel) stage (> 250 h) an apparent increase in ΔA_0 with increasing GPTMS content can be witnessed. It seems to us that additional crosslinking created by the epoxy groups in GPTMS in the xerogels gives rise to more larger pores which are favourable to the ring opening-closure structural change of the dye molecules.

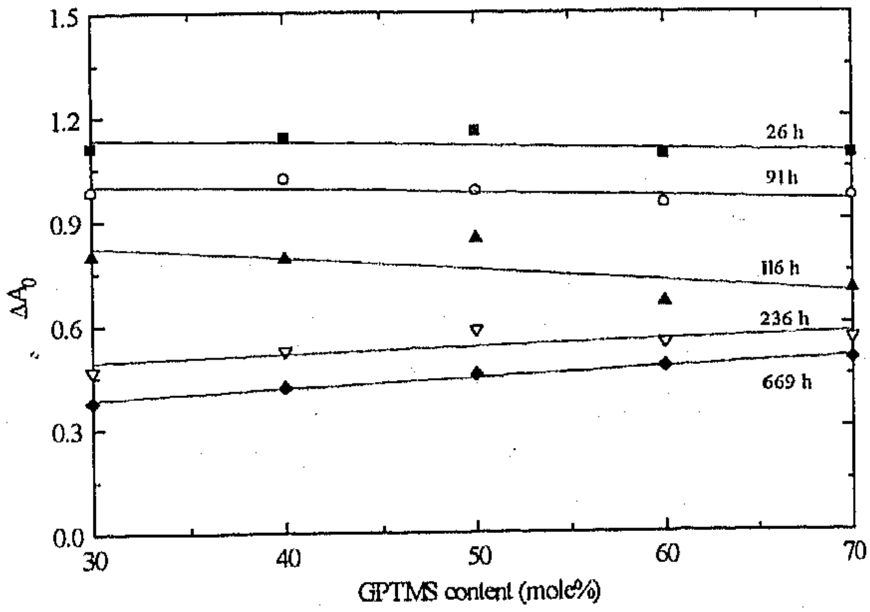

Fig. 3 Photochromic intensity (ΔA_0) of spirooxazine vs. composition in OIHM-EG ($MR_{NaF} = 2\times10^{-4}$) during the sol-wetgel-xerogel transformation

Previous research work on spirooxazine indicates that the polarity of the solvent greatly affects the photochromic intensity of the coloured form. Generally speaking, the higher the polarity of the solvent the higher is the photochromic intensity. OH-group-containing solvents like ethanol possess higher polarity and are advantageous to achieving a higher photochromic intensity. But unfortunately, both the heat treatment stability and the photochemical stability are very disappointing.

The utilization of sol-gel derived gel matrix for spirooxazine has greatly improved the heat treatment stability and photochemical stability[5] but the photochromic intensity (ΔA_0) of the thin coatings (< 10 μm) is not high enough for practical applications because of the decrease in ΔA_0 during the sol-wetgel-xerogel transformation as revealed above. One reason for this is the decrease of the polarity of the environment surrounding the dye molecules due to the decrease in the content of OH-groups resulted from further polycondensation in the gels. In this work, we introduce bisphenol-A (BPA) into the OIHM aimig to enhance the photochromic intensity.

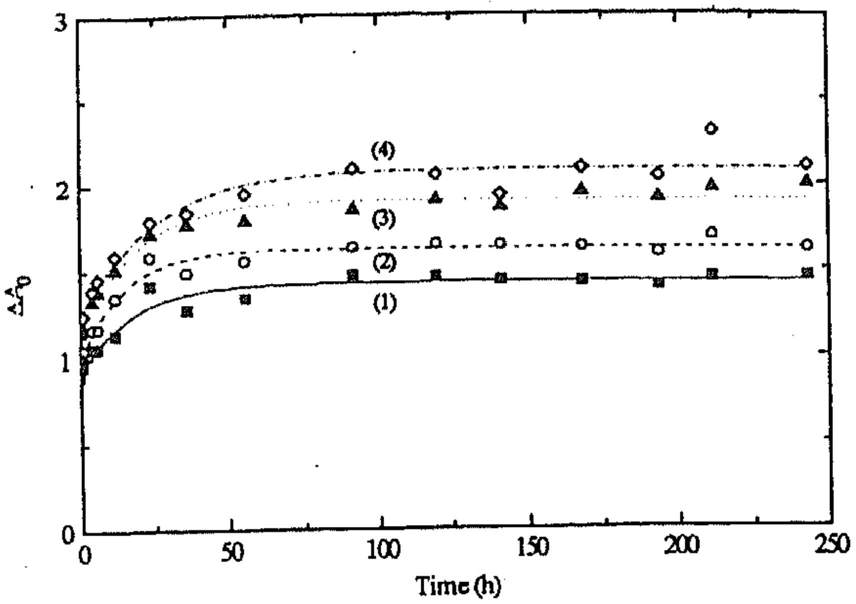

Fig. 4 Variation of photochromic intensity (ΔA_0) of spirooxazine in OIHM-EG37 during the sol-gel transformation at different content of bisphenol-A (MR_{BPA}): (1) 0.15, (2) 0.20, (3) 0.25, (4) 0.30

In Fig. 4, variation of ΔA_0 of spirooxazine in OIHM-EG37 containing different amount of BPA during the sol-gel transformation is depicted. It is apparent that ΔA_0 increases in the sol-wetgel stage (< 100 h) and levels off in the wetgel-xerogel stage. The higher the content of BPA, the higher the equillibrium ΔA_0. The sensitization of ΔA_0 by BPA is encouraging to aquiring suffiently high photochromic intensity even in the case of thin coatings (< 10 μm).

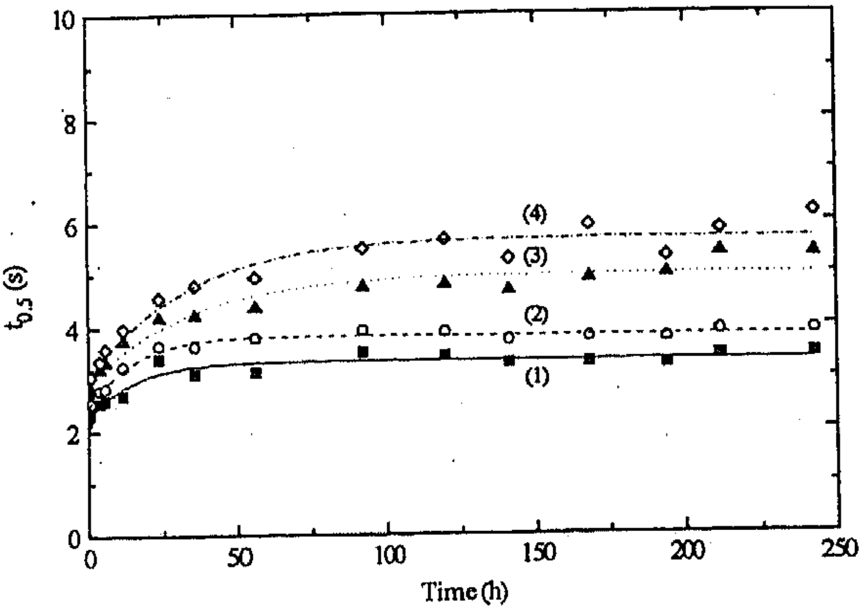

Fig. 5 Variation of half-life time ($t_{0.5}$) of spirooxazine in OIHM-EG37 during the sol-gel transformation at different content of bisphenol-A (MR_{BPA}): (1) 0.15, (2) 0.20, (3) 0.25, (4) 0.30

$t_{0.5}$ of spirooxazine increases with increasing BPA content, too, as Fig. 5 shows. The higher the content of BPA, the higher the equilibrium $t_{0.5}$. This is because the steric hindrance to the dye molecules increases with increasing BPA content. However, the maximum $t_{0.5}$ is less than 6 s, which is much lower than in polymer matrix (ca. 100 s) and more than enough meets the requirements for practical applications.

Conclusions

Using sol-gel derived organic-inorganic hybrid materials as solid matrices for photochromic spirooxazine dye, we can maintain the photochromic properties (ΔA_0, $t_{0.5}$) at a stable and reasonably high level in the xerogels.

The addition of bisphenol-A greatly enhances the photochromic intensity while leads to an acceptable increase of half-life time. This makes it possible to produce coatings (< 10 μm) with high photochromic intensity and satisfactorily high fading speed.

References

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